SOME DOUBLE HALIDES

OF

MERCURY

THESIS

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JOHN NESBIT SWAN

1893

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ON SOME DOUBLE HALIDES OF MERCURY.

Introduction.

In continuation of the investigations which have been in progress for some years in this laboratory on the so-called double halides, work was begun on the compounds which mercuric chloride forms with the chlorides of the other elements of the second group of the Periodic System. After some months of work upon these, attention was turned to the possibility of forming double salts from the salts of organic bases like aniline and the toluidines; and the following work was done on these compounds. On account of the more satisfactory results of this work arising from the greater ease of formation and purification of the compounds formed, the description of these will be given first,—the description of the inorganic mercurates being left for the latter part of the paper.

Historical.

Some double halides of metals with the halides of aromatic organic bases have been prepared and described. Destrem[1] repared an aniline chlorocuprate ($Cu\ Cl_2\ 2\ (C_6H_5NH_3Cl)$) by adding aniline hydrochloride to an alcoholic solution of cupric chloride. This he describes as a well behaved salt.

Bibanow[2] prepared an orthotoluidine chlorozincate ($(C_7H_7NH_3Cl)_2Zn\ Cl_2$) by bringing together a concentrated zinc chloride solution and orthotoluidine hydrochloride and crystallizing at a temperature of —5°.

Widmann[3] describes a metatoluidine chloroplatinate ($(C_7H_7NH_3Cl)_2Pt\ Cl_4$). These salts are also described:

$(C_7H_7NH_3Cl)_2Zn\ Cl_2$ (p).[4]
$(C_6H_5NH_3Cl)_2Sn\ Cl_4$.[5]
$(C_7H_7NH_3Cl)_2Sn\ Cl_4$.[5]
$(C_7H_7NH_3Cl)Pt\ Cl_4$.[6]

[1] Bull. Soc. Chim. 30, 482.
[2] Jahrs. 1874, 747.
[3] Ber. 13, 677.
[4] Grafinghoff, Zts. Ch. 1865, 599.
[5] Hjortdahl, Zeits Kryst 6, 490
[6] Muspratt Hoffman, Ann. 54,16.

The platinum salt $C_6H_5NH_3Cl.\ PtCl_4$ was made by Hofmann[1] by bringing together aniline, hydrochloric acid, and platinic chloride. After describing this salt he proceeds to make a mercury salt, but does not proceed in the same manner, and therefore gets a salt of a different nature, viz : aniline mercuric chloride. (''Kyanolquecksilberchlorid''). In speaking of the properties of this he says : ''Auch von Chlorwasserstoffsäure wird es gelöst. Hat man zu wenig Salzsäure zugesetzt, so schmilzt der ungelöste Theil beim erwärmen zu einem rothen Oele, welches den Boden der Röhre bedeckt. Durch Zusatz von mehr Salzsäure erhält man aber wieder eine klare Lösung aus der sich beim erkalten schöne weisse Krystalle absetzen. Ich weiss nicht ob diess die unveränderte Quecksilberverbindung ist oder ob Chlorwasserstoffsäure in die Zusammensetzung aufgenommen wurde.

The corresponding iodides, bromides, and cyanides of mercury and other metals are described in a few instances, e. g.:

$BiI_3C_6H_5NH_3I.$[2]

$Hg(CN)_2C_6H_5NH_3CN.$[3]

No investigation seems to have been made with the idea of preparing two or more series of salts with the same metal, such e. g. as $C_6H_5NH_3Cl\ M''\ Cl_2$, $C_6H_5NH_3Cl_2M''Cl_2$, etc. The salts were made by simply bringing solutions together with no particular care as to proportions so that a precipitate was formed immediately or on cooling. Of course at the time this work was done there was no reason for making any investigation of this kind. It was simply an open field and no classification was attempted, the only generalization being, ''It has the power to form double salts.''

Wells[4] describes a new class of double salts of the general formula $M'_3M''Hl_5$ or $3M'Hl,\ M''Hl_2$. Although, judging from the analyses given, he did not succeed in preparing very pure specimens of these salts, yet the crystallographic description given by Penfield taken with the description of the salts indicates their reality. The difficulty of the preparation of pure specimens and their recrystallization from a solvent has interfered with the investigation of the possibility of the preparation of salts of this class and other classes such as $4M'Hl.\ M''Hl_2$, etc.

[1]An. 47, 62. [2]Kraut. Ann. 210, 323. [3]Claus & Merck. Ber. XVI. 2737. [4]Am. Jr. Sci. 44, 222.

The present class of compounds seemed to be free from this great difficulty to a large degree, and therefore strenuous efforts were made to prepare compounds of the above classes, but in all cases without success, as will be shown later. This is no argument, however, as to the existence of such compounds, because these bases vary among themselves as to the classes of compounds formed. This fact gave rise to a great deal of work in the endeavor to get uniform classes of salts with each base. Another question of interest at this time in this line of work is in regard to the possibility of the formation of mixed double halides. Can a salt like $M'M''(Cl)_2Br$ or $M'M''(ClBr)Cl$ exist? Wells[1] showed the existence of compounds like $Cs(Cl)_2Br$ and used Remsen's hypothesis in their explanation, viz: That two halogen atoms play the part of an oxygen atom. He is led to the conclusion that this couplet can consist of different atoms. In the article above cited[2] Wells describes the preparation of mixed double halides. Here again the difficulty of procuring definite products interfered with the exactness in results which one might desire, but there seems to be good evidence of the existence of these salts.

Before this work, Atkinson had described these salts[3]:

$$K_3SbCl_3Br_3I_2H_2O.$$

$$SbCl_3BrKH_2O.$$

Pitkins[4] described the salt $2KBr.PtCl_4$. Remsen and Richardson[5] working with potassium tin salts were led to the conclusion that the existence of a pure mixed salt of potassium and tin was doubtful. Later, Herty[6] describes his fruitless endeavors to prepare mixed double halides with lead and potassium.

During the time that the work on the chlorides about to be described was in progress work was prosecuted on the attempt to prepare mixed halides. Mercuric bromide was used with the chlorides of the organic bases in each case. Many crops of crystals were obtained—sometimes three sets of them in the same beaker, and for some time it seemed a hopeless task to attempt to get anything definite, but, after many failures, some uniform crops of crystals were obtained at last, and these proved to be mixed double halides.

[1]Am. Jr. Sci. 43.
[2]Am. Jr. Sci. 44, p. 232.
[3]Jr. Chem. Soc. 43 (1883) 289.
[4]Chem. News 47, 118.
[5]Am. Chem. Jr. 14, 96.
[6]Am. Chem. Jr. 15, 81.

The following salts are described in this paper :

Aniline Salts—

$C_6H_5NH_3Hg_2Cl_5$.
$C_6H_5NH_3HgCl_3$.
$(C_6H_5NH_3)_2HgCl_4$.

Orthotoluidine Salts—

$C_7H_7NH_3Hg_2Cl_5$.
$C_7H_7NH_3HgCl_3$.
$(C_7H_7NH_3)_2HgCl_4$.

Metatoluidine Salts—

$C_7H_7NH_3Hg_2Cl_5$.
$C_7H_7NH_3HgCl_3$.
$(C_7H_7NH_3)_2HgCl_4$.

Paratoluidine Salt—

$C_7H_7NH_3HgCl_3$.

Mixed Salt—

$C_7H_7NH_3HgBr_2Cl$.

Inorganic Salts—

$MgHg_3Cl_8+6H_2O$.
$SrHg_3Cl_8+(H_2O)x$.
$BaHg_3Cl_8+8H_2O$.

It will be noticed that among the organic salts the class $BHClHgCl_2$ is the only one found with all four bases—the classes $BHCl.2HgCl_2$ and $2BHCl.HgCl_2$ being found with all except paratoluidine. (B being used to represent a base, as aniline).

Naming of Compounds.—No complete system of naming of the double halides has yet been adopted. The first and second aniline salts are easily named, thus : dianiline chloromercurate, and aniline chloromercurate. The third might be called aniline dichloromercurate or aniline chlorodimercurate. In this paper the former will be used and the analogous names in case of the toluidine salts.

Methods of Analysis.—In making analyses of these salts chlorine and mercury only were determined. The estimation of

mercury was made by precipitation as sulphide. This required some time for complete precipitation as sulphide, owing to the fact that a yellow, or yellowish white, precipitate of sulphochloride is first formed and care must be taken to have this completely changed over to the sulphide. Some free sulphur is sometimes precipitated which can usually be dissolved by washing the precipitate with alcohol and then with carbon bisulphide. In making mercury determinations the solutions were acidified with hydrochloric acid. The filters used were washed, dried and weighed before using, and then the precipitate was weighed on the filter, and the weight of the latter deducted. Satisfactory results were obtained by this method with pure mercuric chloride as a test of the method. Some of the determinations were made in a Gooch crucible. The drying of the precipitates was conducted in an air-bath kept near 90°. Greater difficulty was experienced in getting a satisfactory method for the estimation of chlorine. Owing to the fact that it cannot be estimated in presence of mercuric chloride,[1] it was necessary to remove the latter. This was done with hydrogen sulphide. Then the problem of getting out the excess of the latter was to be solved, as it could not be driven off by heat for fear of losing some hydrochloric acid at the same time. After trying several methods it was finally removed as free sulphur by the addition of ammonium ferric alum to the solution and letting stand for some hours, and then filtering. Chlorine was then precipitated as silver chloride and weighed in a Gooch crucible. This was found to work fairly satisfactorily, but required care in freeing the material used from chlorine, and it usually gave high results. In some of the work on the inorganic salts, chlorine was estimated volumetrically, but the gravimetric method gave more satisfactory results owing to a gradual change of the standardized solutions with lapse of time. The salts for analysis were purified by treatment with animal charcoal, and recrystallization from water acidified with hydrochloric acid.

[1] See Fresen. Quant. Analyse. 1, 473.

Aniline Salts.

Aniline Dichloromercurate.—($C_6H_5NH_3Hg_2Cl_5$).

Following Destrem's method, aniline hydrochloride was added to an alcoholic solution of mercuric chloride. A salt was formed in irregular crystals while the solution became much colored and some kind of decomposition had evidently taken place which interfered with the purity of the product. The same experiment was performed using a water solution instead of alcohol. 9 grams of aniline hydrochloride were dissolved in warm water, 20 grams of mercuric chloride were added, and the whole heated and filtered. A salt began to crystallize almost as soon as the beaker had begun to cool. This salt was freed from the mother-liquor and washed with water on the filter-pump. The salt which was formed in alcohol was recrystallized from hot water. Determinations of mercury in both indicated the same compound, viz: aniline dichloromercurate ($C_6H_5NH_3Hg_2Cl_5$). In the meantime work on the water solutions, which will be given later in the description of the paratoluidine salt, was done, and solutions acidified with hydrochloric acid were used after this. Following these suggestions, aniline hydrochloride and mercuric chloride were mixed in a beaker in molecular quantities for the above salt; then water and a little hydrochloric acid added, and the whole heated to boiling. A beautiful white salt in sheaves, sometimes in rosettes, crystallized on cooling. The salt was well washed with cold water on the filter-pump and recrystallized from acidified water solution after treatment with animal charcoal.

The salt was analyzed for mercury and chlorine with the following results:

1.	0.6727	gram salt	gave	0.4651	gram	HgS.
2.	0.4727	" "	"	0.3263	"	"
3.	0.7735	" "	"	0.8307	"	AgCl.
4.	0.8180	" "	"	0.8784	"	"

	Calculated % for $C_6H_5NH_3Hg_2Cl_5$	Found 1.	2.	3.	4.
Hg.	59.62	59.60	59.51		
Cl.	26.38			26.56	26.55

In the first preparation the salt was found when the aniline hydrochloride was in excess, and the solution boiled. Repeated trials showed that the best results were obtained when mercuric chloride was present in slight excess.

Properties.—Aniline dichloromercurate is much more readily soluble in hot than cold water, being rather insoluble in the latter. It is much more soluble in methyl and ethyl alcohols. It is only slightly soluble in ether. When boiled for some time with alcohol it is decomposed to some extent. Heating to boiling in pure water does not decompose it, although continued boiling may do so. The salt is stable in the air if dry, but becomes discolored like many aniline salts if exposed for some time in a moist condition.

Aniline Chloromercurate.—($C_6H_5NH_3HgCl_3$).

Having obtained this aniline compound in the above manner, the attempt to prepare compounds having a larger, and those having a smaller, proportion of mercuric chloride was next in order. With this end in view, a larger proportion of mercuric chloride was added to constant quantities of aniline hydrochloride. This was carried on until the mercuric chloride would crystallize out with the salt described, and no compound containing a larger proportion of mercuric chloride was obtained. Gradually diminishing the proportion of mercuric chloride, a salt differing from the above was obtained when molecular quantities of the chlorides were mixed and the solution not heated too strongly. It was found, however, that there was a tendency to pass to the first form when the solution of equal molecular quantities was boiled. By using a slight excess of aniline hydrochloride the new salt was obtained in better form. The salt was recrystallized from acidified water solution, washed with water on the filter-pump, and dried.

The analyses for mercury and chlorine of the purified salt gave the following results :

1. 0.7509 gram salt gave 0.4365 gram HgS.
2. 0.9662 " " " 0.5585 " "
3. 0.5662 " " " 0.6114 " AgCl.
4. 0.7075 " " " 0.7604 " "

	Calculated % for $C_6H_5NH_3HgCl_3$	Found 1.	2.	3.	4.
Hg.	49.98	50.11	49.83		
Cl.	26.54			26.70	26.58

This salt was obtained from ethyl alcohol and from methyl alcohol solutions just as from water solutions. In all cases a small quantity of hydrochloric acid was added. Attempts were made to get finer and larger crystals by using the alcohols and allowing the solutions to evaporate gradually, but with only partial success. The solutions in all cases, except one with methyl alcohol, became very much discolored, and a green substance was continually being formed. This was often filtered off and the solution cleared by animal charcoal, but only an impure set of crystals were obtained, where they were obtained at all. The crystals seem to have the same general form, whether obtained from water or alcohol solutions.

Dianiline Chloromercurate.—$(C_6H_5NH_3)_2HgCl_4$.

By using still smaller proportions of mercuric chloride to constant quantities of aniline hydrochloride, a third salt was obtained with a distinct crystalline form. This salt crystallized in bright glistening needles. It is much more soluble in water and dilute acid than the other salts, and for this reason could not be washed as easily without dissolving considerable of the salt, but it was recrystallized.

Analyses gave the following results :

1. 0.4696 gram salt gave 0.2058 gram HgS.
2. 0.7722 " " " 0.8348 " AgCl.
3. 0.6849 " " " 0.7373 " "

	Calculated % for $(C_6H_5NH_3)_2HgCl_4$	Found 1.	2.	3.
Hg.	37.77	37.78		
Cl.	26.75		26.73	26.62

The salt is obtained most readily and without danger of the salt with more mercuric chloride being formed, if aniline hydrochloride is added in excess to the original solution.

Properties.—Dianiline chloromercurate is much more soluble than either of the above described chloromercurates. Concentrated solutions must be used in its preparation. By addition of the proper amount of mercuric chloride and boiling, it can be converted into aniline chloromercurate.

The process of adding a larger proportion of aniline hydrochloride was continued still farther in different proportions, but no other compound was obtained. This last described salt was always formed and then aniline hydrochloride would crystallize out mixed with the crystals of the salt. Repeated attempts with varying conditions of temperature, dilution, acidification, and proportion of ingredients brought the same result. We conclude that a salt with a larger proportion of aniline hydrochloride than is found in dianiline chloromercurate cannot be made by this method. No other method was tried. It was noted sometimes in the heating of the solutions from which the above salts crystallized, and always when they were slowly evaporated by heat, that a flocculent green substance was formed in the solution. This floated about and had to be separated by filtration. Owing to lack of time this has not been investigated and the exact conditions suited to its formation were not learned. It was usually much more abundant in the alcoholic solutions. It was observed that the salts with smaller proportions of mercuric chloride can be converted into those with larger proportions. On the other hand, the latter can be converted into the former by the addition of aniline hydrochloride. This is not as easily accomplished, however, and the aniline chloride must be added in excess and the solution boiled longer. Aniline

dichloromercurate seems to be the most easily formed salt.

The mother-liquors from which these salts crystallized were slowly evaporated to learn if salts of different structure could be formed, but nothing new was so found. Sometimes a second crop of crystals of the salt first formed was obtained, but usually mixtures of the salts or of the salts and the simple chlorides were formed.

Orthotoluidine Chloromercurates.

Orthotoluidine Dichloromercurate.—($C_7H_7NH_3Hg_2Cl_5$).

Following the indications of the experience with the aniline salts, nearly molecular quantities, for the above formula, of orthotoluidine hydrochloride and mercuric chloride were brought together in acidulated water solution, with the mercuric chloride in slight excess. A salt crystallized out on cooling. The first part of the crystallization was in irregular, ragged plates and on top of these a few needles of prism-like crystals were deposited during the night. The two sets of crystals having apparently different solubilities, water was added, the solution heated and allowed to crystallize again, but with the same result. This operation was repeated *in toto* again. A new solution was made and it acted in the same way. One of these solutions was heated and the ragged crystals were again deposited on cooling. The mother-liquor was poured off and the crystals were washed with the aid of the filter-pump. The mother-liquor after a time began to form the prism-like crystals. These were also separated and washed. Determinations for mercury in the two salts indicated that both had the same composition, viz : $C_7H_7NH_3Hg_2Cl_5$. Thinking the different forms of crystals were due to some impurity—possibly some para salt present,—a new start was made. The orthotoluidine first used was marked C. P. Some more of this was taken and treated with oxalic acid, and then by crystallization separated from any possible para salt present. The oxalate was then treated with a base and redistilled with steam. By this means a pure base was obtained and by treatment with pure hydrochloric acid and recrystallization, a most beautiful salt was obtained. On making the double salt, using this chloride, the crystals were deposited in beautiful

leaf-like forms in which the veins extended beyond the border, giving a ragged edge. This was the general form first observed. There seemed to be no tendency to form the other crystals in this case. The salt was then recrystallized and purified and analyzed with the following result:

1. 0.5973 gram salt gave 0.4054 gram HgS.
2. 0.6948 " " " 0.4703 " "
3. 0.6740 " " " 0.7096 " AgCl.
4. 0.9160 " " " 0.9663 " "

	Calculated % for $C_7H_7NH_3Hg_2Cl_5$	Found 1.	2.	3.	4.
Hg.	58.40	58.51	58.35		
Cl.	25.85			26.04	26.09

Orthotoluidine Chloromercurate.—($C_7H_7NH_3HgCl_3$).

Several attempts to make the above, at first, were unsuccessful. In fact, it was first obtained by evaporating the mother-liquor from a crystallization of orthotoluidine dichloromercurate in which the organic chloride was in excess. By using a slight excess of the toluidine chloride and only heating to the boiling-point the salt was obtained.

Analyses of the purified salt gave these results:

1. 0.5802 gram salt gave 0.3247 gram HgS.
2. 0.5724 " " " 0.3194 " "
3. 0.7748 " " " 0.8111 " AgCl.
4. 0.6999 " " " 0.7313 " "

	Calculated % for $C_7H_7NH_3HgCl_3$	Found 1.	2.	3.	4.
Hg.	48.30	48.24	48.10		
Cl.	25.65			25.89	25.84

Properties.—This salt in regard to its solubility and general properties is very much like the corresponding aniline salt.

Diorthotoluidine Chloromercurate.—($(C_7H_7NH_3)_2HgCl_4$).

This salt was readily formed by bringing the ingredients together in about the calculated proportions for the formation of the salt, but with the organic chloride in slight excess. A *small* amount of acidulated water must be used as the salt is quite soluble in cold water. It is not so readily purified as the others on account of the fact that it is so soluble as to preclude much washing. The salt crystallizes in bright, glistening needles or prisms which are usually collected in rosettes. It is quite soluble in alcohol, and soon colors the solution on heating, showing decomposition. This is characteristic of the chlorides of the formula $(BH)_2HgCl_4$. They seem less stable than the halides with a larger proportion of mercuric chloride.

Analyses of the purified salt gave:

1. 0.5552 gram salt gave 0.2333 gram HgS.
2. 0.6308 " " " 0.2637 " "
3. 0.4591 " " " 0.4780 " AgCl.
4. 0.5974 " " " 0.6169 " "

	Calculated % for $(C_7H_7NH_3)_2HgCl_4$	Found 1.	2.	3.	4.
Hg.	35.88	36.22	36.04		
Cl.	25.41			25.75	25.54

The properties of the orthotoluidine salts are much the same as those of the corresponding aniline salts. The intermediate salts are more difficult of preparation than the others because of the ease with which they pass to the salt with more mercury on the one hand, and the liability of the formation of some of the salt with a less amount of mercury on the other. As in the case of the aniline salts, the toluidine salts become discolored on standing only a short time in solution. In the formation of dianiline chloromercurate and diorthotoluidine mercurate, particularly, is this the case. With these the flocculent green substance before mentioned was most abundant. As before, attempts were made to get a salt with a larger proportion of the

organic chloride but without success, although many efforts were made. There were no indications of a fourth salt in any case. Some beautiful six-sided plates were often formed, but these always proved to be pure orthotoluidine hydrochloride.

Metatoluidine Salts.

Metatoluidine Dicholoromercurate.—($C_7H_7NH_3Hg_2Cl_5$.)

The metatoluidine hydrochloride was not so carefully purified as were the other chlorides. The above salt was readily obtained in the same manner as the corresponding salts already described. It was purified in the usual manner and analyzed with these results:

1. 0.4198 gram salt gave 0.2856 gram HgS.
2. 0.5938 " " " 0.4027 " "
3. 0.4954 " " " 0.5207 " AgCl.
4. 0.4874 " " " 0.5119 " "

	Calculated % for $C_7H_7NH_3Hg_2Cl_5$	Found 1.	2.	3.	4.
Hg.	58.40	58.65	58.46		
Cl.	25.85			25.99	25.97

Properties.—Metatoluidine dichloromercurate crystallizes in thin plates or scales. It is very much like the corresponding aniline and orthotoluidine salts in solubility and other properties. The meta salt seems less soluble than the others. The crystallization took place soon after the solution began to cool—a certain temperature rather than a certain concentration of solution seeming to determine the point of saturation. The salt would all crystallize near this temperature. This was true of solutions of quite different concentration.

Metatoluidine Chloromercurate.—($C_7H_7NH_3HgCl_3$).

The amount of metatoluidine at hand did not permit of as thorough an investigation of this salt as was given to those before described. This intermediate salt is the only one which

suffered, however, from lack of material. It is the most difficult to form, and therefore required more of the ingredients used. One or two crops of crystals were obtained in small quantity which had a satisfactory appearance, and these gave analyses for this salt. They were not recrystallized, however, and the analyses below are of specimens from these crystallizations. The crystals which had a light purplish color (probably due to impurities) formed in very thin plates which reached across the beaker and which broke up into scales when taken out.

Analyses of the specimens gave the following results:

1. 0.4126 gram salt gave 0.2289 gram HgS.
2. 0.4906 " " " 0.2737 " "
3. 0.5730 " " " 0.6031 " AgCl.
4. 0.6486 " " " 0.6774 " "

	Calculated % for $C_7H_7NH_3HgCl_3$	Found 1.	2.	3.	4.
Hg.	48.30	47.82	48.13		
Cl.	25.65			26.03	25.83

Dimetatoluidine Chloromercurate.—$((C_7H_7NH_3)_2HgCl_4)$.

This salt was made in the usual way. It crystallized in thin glistening scales with greyish lustre. Little need be said of it as it resembles closely the corresponding salts already described.

Analyses of the purified salt gave these results:

1. 0.4316 gram salt gave 0.1801 gram HgS.
2. 0.5152 " " " 0.2147 " "
3. 0.4844 " " " 0.5004 " AgCl.
4. 0.4851 " " " 0.5002 " "

	Calculated % for $(C_7H_7NH_3)_2HgCl_4$	Found 1.	2.	3.	4.
Hg.	35.88	35.97	35.92		
Cl.	25.41			25.55	25.55

Paratoluidine Chloromercurate.—($C_7H_7NH_3HgCl_3$).

Paratoluidine hydrochloride was made in the usual way and purified by recrystallization from acidified water solution. The work with paratoluidine was begun about the same time as that with aniline, and therefore before the three classes were known to exist. About molecular quantities of the two chlorides were weighed into a beaker and water added. On heating gradually, a salt suddenly separated out which completely filled the space occupied by the liquid. This was dissolved on further heating and the salt crystallized out on cooling. As there was some doubt as to the homogeneousness of the crystallization, much more water was added and a second crystallization was made. This appeared to have two sets of crystals, one more soluble than the other.

By adding more water and watching the process of separation of the crystals, the less soluble salt was obtained. A determination of mercury indicated the salt $C_7H_7NH_2HgCl_2$. Other trials seemed to indicate that a pure uniform salt could not be obtained with water alone. It either decomposed the salt formed or caused the action to proceed in such a manner as to form more than one salt. It was here found that, if the solutions were acidified with hydrochloric acid, uniform crystallizations could be obtained. Following the suggestion of these experiences, the salt was made by bringing together molecular quantities of paratoluidine hydrochloride and mercuric chloride. Water and a little hydrochloric acid were added and the whole gently heated. In a few minutes a precipitate was formed which pervaded the whole solution. On higher heating this dissolved, and readily crystallized on cooling in beautiful white needles. The needles were usually collected into sheaves or rosettes, but were sometimes alone. The salt was usually colored unless the solution was treated with charcoal before crystallizing.

Analyses of the purified compound were made with the following results :

1. 0.7092 gram salt gave 0.3987 gram HgS.
2. 0.2581 " " " 0.1454 " "
3. 0.6195 " " " 0.6456 " AgCl.
4. 0.6567 " " " 0.6867 " "

	Calculated % for $C_7H_7NH_3HgCl_3$	Found 1.	2.	3.	4.
Hg.	48.30	48.46	48.56		
Cl.	25.65			25.77	25.86

Properties.—Paratoluidine chloromercurate is much more soluble in hot than cold water and can, therefore, be readily crystallized. It is more readily soluble in methyl and ethyl alcohols, but is insoluble in ether. The salt can be washed very thoroughly with cold water on the filter-pump, and this method was used. It was dried by pressing between layers of drying paper. By crystallizing slowly, beautiful needles nearly three inches long were obtained. On exposure for a little time in the air of the laboratory in a moist condition they assume a rose tint, and become more discolored on longer standing. When thoroughly dried they assume a very slight brownish or cream tint on standing in a weighing tube.

Next a solution of the original chlorides in proportion of one molecule of paratoluidine hydrochloride to two of mercuric chloride was made, when the same salt was obtained. This solution was boiled for some time, and solutions with these proportions of chlorides and with varying amounts of hydrochloric acid were made, but the same results were always obtained. A salt of the composition $C_7H_7NH_3Hg_2Cl_5$ in the cases of the ortho and meta compounds and a corresponding aniline salt having been obtained, strenuous efforts were made to get a similar para compound by these methods. The excess of mercuric chloride was gradually increased in successive trials until it began to crystallize out with the salt originally obtained, mixed with it. It seemed strange that in each of the other cases a compound containing one molecule of the basic chloride to two of the mercuric chloride could be obtained,

while with the para compound it could not be formed. It could not be obtained by these methods, however, although the conditions were varied through wide ranges as to the excess of mercuric chloride, the amount of water used, the amount of acid added, and the degree of heat employed. This fact suggested the idea that there might be a greater possibility in the other direction with the para compound than with the ortho and meta, viz: that not only would a compound of the composition $(C_7H_7NH_3)_2HgCl_4$ be formed, but also a possibility was suggested of going still farther in the proportion of the basic chloride to the mercuric chloride. With this in view experiments were next made using an excess of the basic chloride in gradually increasing amounts and under varying conditions. The results were invariably the same. The salt above described was formed in every case in quantity sufficient to use up the mercuric chloride and on evaporation the excess of paratoluidine hydrochloride crystallized from the solution. $C_7H_7NH_3HgCl_3$ is therefore the formula for the only paratoluidine chloromercurate which it seems possible to make by these methods. This para salt, on account of its insolubility in cold water and the ease with which it can be crystallized, was probably the most satisfactory of the salts obtained. In its formation it was free from any admixture of the salts having different proportions of the chlorides—a fact which gave trouble, sometimes, working with the other salts.

Summary.

1. These salts were found:
   Aniline dichloromercurate, $C_6H_5NH_3Hg_2Cl_5$;
   Aniline chloromercurate, $C_6H_5NH_3HgCl_3$;
   Dianiline chloromercurate, $(C_6H_5NH_3)_2HgCl_4$;
   The corresponding ortho- and metatoluidine salts and paratoluidine chloromercurate.

2. The corresponding salts of aniline, metatoluidine and orthotoluidine are very much alike in method of formation and in general properties, but differ somewhat in crystalline form.

3. The only paratoluidine salt formed is in properties much like the salts of the other bases which have a larger proportion of mercuric chloride.

4. Only these salts were obtainable by this method.

Mixed Double Halides.

No complete investigation has been made in this line, but work is still in progress. A few words will be given in order to show the nature and tendency of the work.

4 grams of orthotoluidine hydrochloride and 12 grams of mercuric bromide were weighed into a beaker with about 75 c. c. of water, and a few drops of hydrochloric acid added. (Numerous attempts with water only were failures). Some mercuric bromide crystallized out and was removed. On longer standing a salt crystallized in beautiful, glistening needles. These were uniform and regular in appearance, and were washed and dried.

Analyses for mercury gave :

I. 40.11% II. 40.51%

Calculated for $C_7H_7NH_3HgBr_2Cl$, Hg 39.76%.

The existence of mixed halides of this order seems undoubted. The only difficulty is to get them in good condition. The above is given to show the possibility of their formation.

When a chloride and bromide of the above kinds are mixed there are a number of possibilities—any of these salts may be formed : $HgBr_2$, $HgCl_2$, $C_7H_7NH_3HgBrCl_2$, $C_7H_7NH_3HgBr_2Cl$, and several others which might crystallize out. In some of the experiments all these possibilities seemed to be realized in the same beaker, judging from the various crystals formed.

Some of the salts when heated in the mother-liquor melt to heavy oils which sink to the bottom of the beaker. These oils crystallize on cooling, but their nature has not been fully investigated. At present the most that can be said is that there is no doubt in the mind of the author as to the existence of the mixed salts, and the work on them will be continued.

Chloromercurates of Elements of the Second Group.

The following salts have been described by von Bonsdorff[1]

Mg.	Ca.
$HgCl_2$. $MgCl_2+6H_2O$.	$2HgCl_2$. $CaCl_2+6H_2O$.
$3HgCl_2$. $MgCl_2+5H_2O$.	$5HgCl_2$. $CaCl_2+8H_2O$.
Zn.	**Sr.**
$HgCl_2$. $ZnCl_2+4H_2O$.	$2HgCl_2$. $SrCl_2+2H_2O$.

Ba.

$2HgCl_2$. $BaCl_2+2H_2O$.

Analyses are given for all except the zinc and strontium salts. The general method of preparation used by von Bonsdorff was to add mercuric chloride, as long as it would dissolve in the cold, to a saturated solution of the other chloride in water. Then by slow evaporation he would obtain two salts from the same solution, the second crystallizing after the first had been removed. His analyses were performed in a tube or bulb prepared for the purpose. The method in general was this: A weighed quantity of the salt to be analyzed was placed in this weighed bulb, and heated to drive off the water of crystallization which was collected in a calcium chloride tube and weighed, or allowed to escape, and estimated by the difference in weight of the bulb. Higher heat was now employed and the mercuric chloride driven off and estimated either by difference or by having it sublime in another part of the apparatus. The residue gave the basic chloride. Considering the method, his results agree very well indeed with calculated results. The chief difficulty in the prosecution of this work was, as has been the case with much of the double halide work, to get pure salts. The salts are so very soluble that when they do crystallize it is difficult to know whether you have a uniform salt or not. In this investigation more work was done upon the magnesium salt than upon any other. The methods of preparation were in general those used by Bonsdorff with some variations. The methods of analysis for mercury and chlorine were those given in the earlier part of this paper. Magnesium was precipitated as pyrophosphate, strontium as carbonate, and barium as sulphate.

[1] Pogg. Ann. 17, 115.

Magnesium Salt.—Following Bonsdorff's directions, mercuric chloride was added to a saturated solution of magnesium chloride. This was heated and filtered. On allowing to stand, or on evaporating slowly, a set of crystals were deposited just as Bonsdorff describes them. It is almost impossible to free this salt completely from the mother-liquor. The method pursued was to place it first on the filter-pump, and then quickly remove it and press it between thick folds of drying-paper by means of a press.

The formation of the salt was tried a great many times and a great many products were analyzed. In order to learn whether the water of crystallization could be driven off by heat or not, about a gram of the salt was carefully weighed and put into an air-bath. Heated for 18 hours at not over 105° it lost 20.79% in weight. Continuing the drying for 15 hours more with the temperature at no time above 102° the salt lost 46%.

Another specimen lost 20% while at a temperature of not over 100°. A third specimen lost 12.6% when dried at a temperature of not over 90°.

Mercuric chloride itself lost about 20% dried at 90° or below in 15 hours, and over 65% when at the same temperature for two or three days.

From these experiments it will be seen that it is impossible to determine the water of crystallization by heating. As the salt does not lose its water of crystallization over sulphuric acid it could not be determined in this way. The average of a number of analyses of the better specimens obtained gave the following results :

	Calculated % for $MgHg_3Cl_8+5H_2O$	Calculated for $MgHg_3Cl_8+6H_2O$	Found
Hg.	60.18	59.11	59.22
Mg.	2.40	2.36	2.58
Cl.	28.41	27.90	27.02

Bonsdorff's analyses calculated with the same atomic weights give:

I. Hg. 60.08%, Mg. 2.46%, Cl. 28.52%.
II. Hg. 59.68%, Mg. 2.43%, Cl. 28.28%.

From these figures he gives the formula with five molecules of water. The formula with six molecules, as is seen, agrees better with the results obtained at this time, but the results are not sufficiently accurate to say with certainty that it has six molecules of water. Bonsdorff describes a salt obtained by evaporation of the mother-liquor from this salt. No such salt was obtained, although many and varied attempts were made to obtain it. Solutions were evaporated slowly for days, others more slowly for weeks, and others still more slowly for months, and no such salt was formed. After the first salt ceased to separate in good form all other crystallizations were mixtures of such a nature as to preclude separation. They were, as nearly as could be learned, mixtures of the first salt and one of the chlorides added in the first place. Attempts were also made to form other salts by using varying proportions of the other two chlorides and by varying the amount of acidification and of dilution, etc.—all with no success.

Some investigations were begun on the chlorides of the other elements of the group. On account of the unfinished condition of the work, only the compounds of strontium and barium will be mentioned.

Strontium Salt.—The chlorides of strontium and mercury were brought together as in making the magnesium salt. A crystallized salt was obtained which is very soluble. It crystallizes in transparent plates, but sometimes in very delicate needles or hairs which project from the top of the solution. This latter was the case when a solution at the point of saturation stood in the air. In the morning there would be a crop of these hairs which would dissolve by the heating of the room during the day and re-form again in the night.

Four analyses of good specimens of this salt gave:

Hg. I. 50.48%. II. 50.59%. III. 50.49%. IV. 50.35%.
Sr. I. 8.90%. II. 8.94%. III. 9.22%. IV. 9.13%.

The salt loses water over calcium chloride or sulphuric acid.

Several weighed specimens left for some days over sulphuric acid lost from 13.30% in the case of the smallest amount to 14.16% in the case of the largest. Bonsdorff gives $SrCl_2 2HgCl_2 + 2H_2O$ as the composition of this salt, but the conclusion arrived at in this work was that it is a compound of the same order as the magnesium salt, viz : $SrHg_3Cl_8 + (H_2O)x$.

No other salt was obtained, although a number of attempts were made to form one.

Barium Salt.—A barium salt was formed in the same manner. This, like the strontium salt, lost water even on standing in the air, so that it had to be analyzed immediately after formation. Two specimens were analyzed after recrystallization with these results :

I.	Hg. 51.87%.	Barium, 11.84%.
II.	Hg. 51.63%.	Barium, 11.89%.

Calculated for $BaHg_3Bl_8 + 8H_2O$, is :

Mercury, 51.54% ;
Barium, 11.77.%

This barium trichloromercurate is less soluble than the other salts, and can, therefore, be prepared more easily and surely.

This work indicates a class of salts formed by this group of the general formula $M''Hg_3Cl_8 + (H_2O)x$. The work was most unsatisfactory in general and was in an unfinished condition when attention was turned to the organic salts. Lack of time prevented further work on this group of salts. A few attempts were made to produce a mixed double salt by using mercuric bromide and chlorides of the other elements, but no satisfactory compound was obtained.

General Conclusions.

All the double halides herein described obey Prof. Remsen's law.[1] All attempts to form classes not obeying this law failed. The work on the organic halides virtually opens up a new line of investigation on the double halides which may have much to do towards giving a complete understanding of their structure and a knowledge of the possible classes which may be formed. The existence of mixed double halides has new substantiation. It is hoped that time and opportunity will be given in the future to complete the unfinished work suggested by this paper, and to make further investigations along the line of organic double halides.

In conclusion it gives the author much pleasure to express his sincere gratitude to Professor Ira Remsen, who suggested this line of work, and under whose supervision it has been prosecuted, for the valued instruction received at his hands both in the lecture room and laboratory.

[1] Am. Chem. Jr. 11, 296.

Biographical.

John Nesbit Swan was born at New Jefferson, O., October 14, 1862. His earlier education was obtained in the public schools, and Westminster College, New Wilmington, Pa. Here he received the degree of A. B. in 1886, and A. M. in 1889. He taught in Burlington, Iowa, city schools; Tarkio College, Tarkio, Mo., and his Alma Mater. Three years have been spent in the Johns Hopkins University pursuing advanced studies in chemistry with subsidiary work in physics and mathematics.

To the several instructors with whom he has been associated, Professors Remsen, Morse and Renouf in chemistry, and Dr. Ames in physics, he would hereby tender his sincere thanks for their uniform kindness and helpfulness to him.